

Second-principles simulations of counter-rotating vortices pairs in $\text{PbTiO}_3/\text{SrTiO}_3$ superlattices

Pablo García-Fernández

Skyrmionics, Santa Fe, August 2017



Universidad de Cantabria



Collaborators

Experiment

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Shang-Lin Hsu

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Cantabria University



Jorge Íñiguez
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Pablo Aguado-Puente
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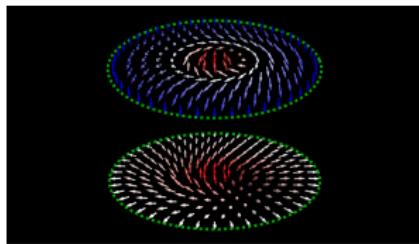


Funding

RyC programme

Spin textures in magnets

$$f = \underbrace{Am^2 \sum_{i,j} (\partial_i n_j)}_{\text{Magnetic stiffness}} + \underbrace{\eta A \left(\vec{\nabla} \vec{m} \right)^2}_{\text{Gradient term}} + \underbrace{f_D(\vec{m})}_{\text{DM Interaction}} + \underbrace{f_0(m)}_{\text{Free energy}}$$

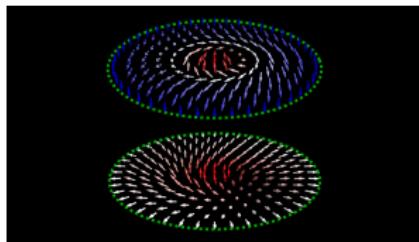


Rich physics (mostly) based on
Dzyaloshinsky-Moriya interactions
Emergent chirality

U. K. Rößler, A. N. Bogdanov and C. Pfleiderer, *Nature*, 442, 797 (2006)

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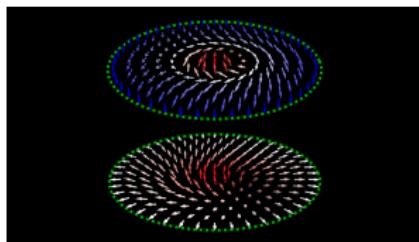
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Main questions for this talk:

- ① Can we find skyrmion-like structures for other ferroics?
Skyrmions without magnetism?

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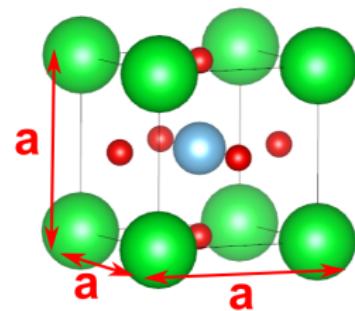
Main questions for this talk:

- ① Can we find skyrmion-like structures for other ferroics?
Skyrmions without magnetism?
- ② Is there an equivalence between spin and dipole moment?
- ③ Can we develop similar structures in ferroelectrics?
Interactions in ferroelectrics?

Main characters: perovskite materials

SrTiO₃, a highly polarizable dielectric

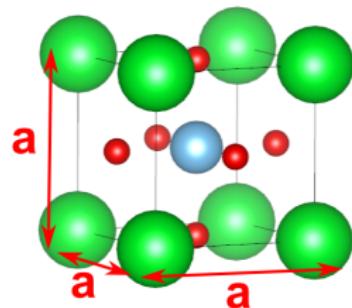
- ▶ Cubic at room temperature
- ▶ Insulator Gap is 3.25eV
- ▶ Paraelectric
Highly polarizable $\varepsilon_r(293K) \approx 300$
- ▶ Ti⁴⁺ is d⁰ → SrTiO₃ DIAMAGNETIC



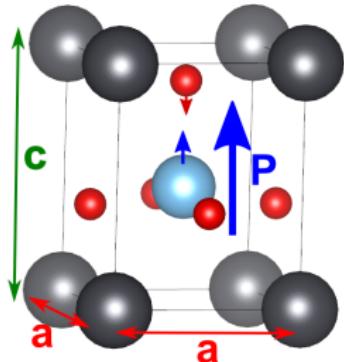
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PbTiO₃, a prototypical ferroelectric



- Tetragonal below 760K
- Insulator Gap is 3.9eV
- Ferroelectric
Polarization switchable below 760K
- Ti⁴⁺ is d⁰ → PbTiO₃ DIAMAGNETIC

Physics of ferroelectric perovskites

Critical size for ferroelectricity

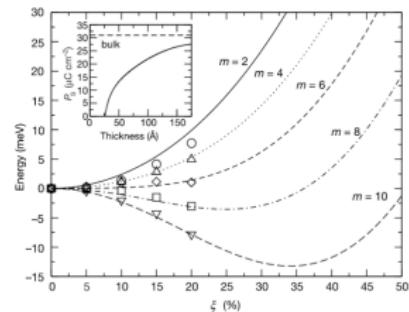
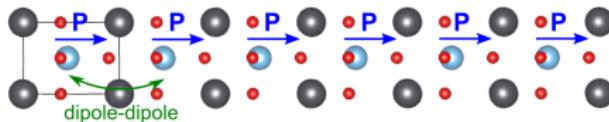
- ▶ Ferroelectric above critical thickness

In unstrained BaTiO_3 $m \sim 6$ unit cells

Junquera and Ghosez, *Nature*, 422, 506 (2003)

- ▶ Origin

Dipole-dipole interactions along chain



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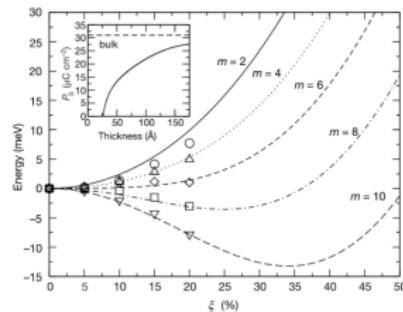
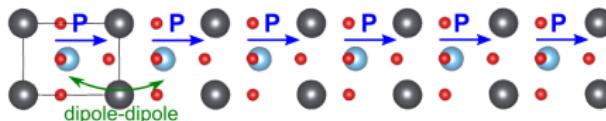
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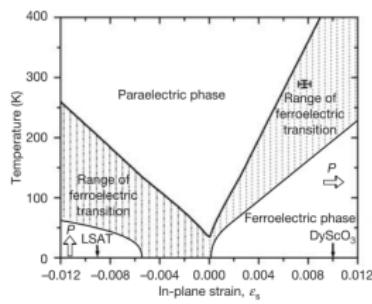
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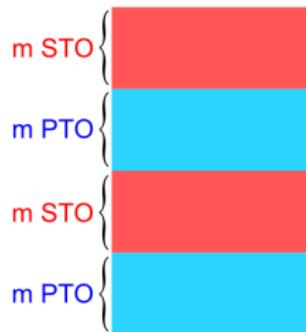
High sensitivity to strains



- ▶ SrTiO_3 and PbTiO_3 are piezoelectric
- ▶ Rich phase diagram under strain
Competition between octahedral rotations and ferroelectricity
- ▶ strained SrTiO_3 becomes ferroelectric
J. H. Haeni et al., *Nature*, 430, 758 (2004)

Ferroelectricity in superlattices

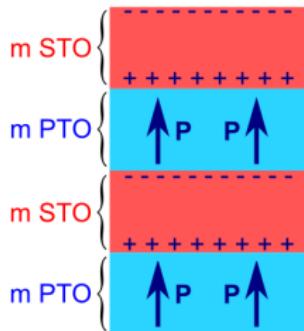
PbTiO_3 and SrTiO_3 can be combined in superlattices



- ▶ Focus on superlattices of periodicity m
 $\text{PTO}_m/\text{STO}_m$
- ▶ PbTiO_3 tends to polarize

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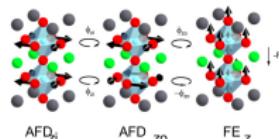
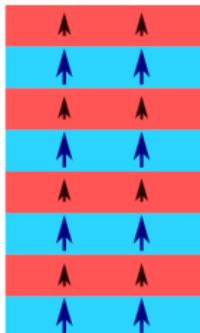
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Two regimes: strong and weak interlayer coupling

- ▶ Short period → Strong coupling

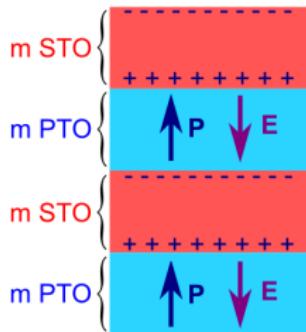


hybrid improper ferroelectricity

Monodomain structure

Ferroelectricity in superlattices

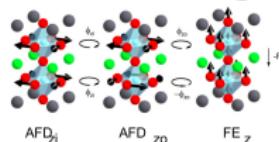
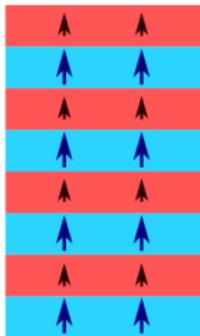
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- ▶ Focus on superlattices of periodicity m $\text{PTO}_m/\text{STO}_m$
- ▶ PbTiO₃ tends to polarize
- ▶ Hindered by less polarizable SrTiO₃
Bound charges create depolarizing field

Two regimes: strong and weak interlayer coupling

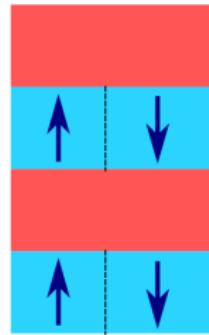
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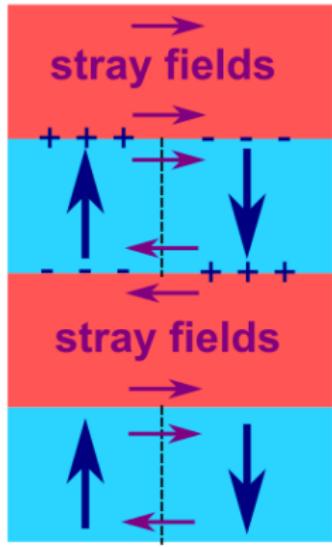
Monodomain structure

- ▶ Long period → Weak coupling
Electrostatics → Multidomain



Appearance of vortexes

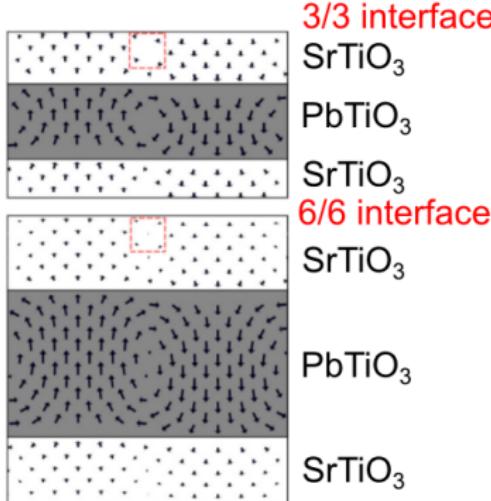
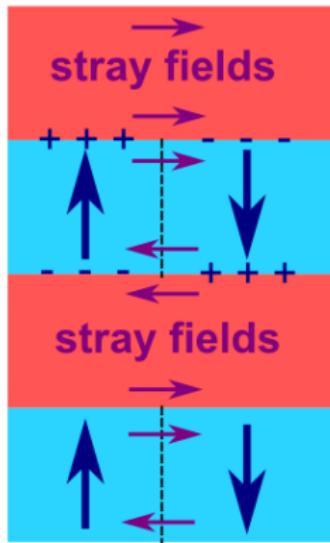
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Appearance of vortexes

In the ideal multidomain structure stray depolarizing fields exist
DFT calculations:

Vortex created to screen stray field



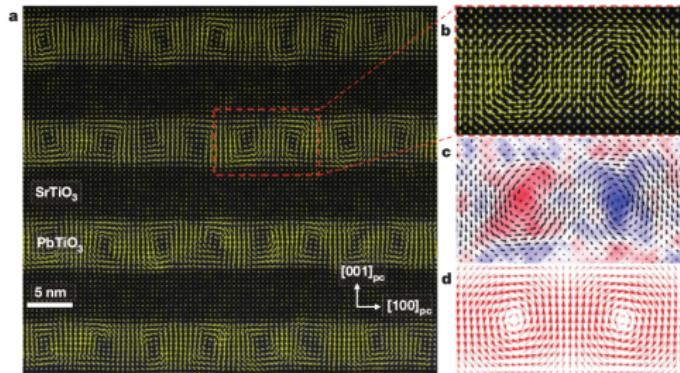
Aguado-Puente and Junquera, *Phys. Rev. B*, 85, 184105 (2012)

What can be observed experimentally?

Experimental observation of ferroelectric vortexes

Clear clockwise/counterclockwise vortex-pairs are observed by:

- ① High-resolution scanning transmission electron microscopy

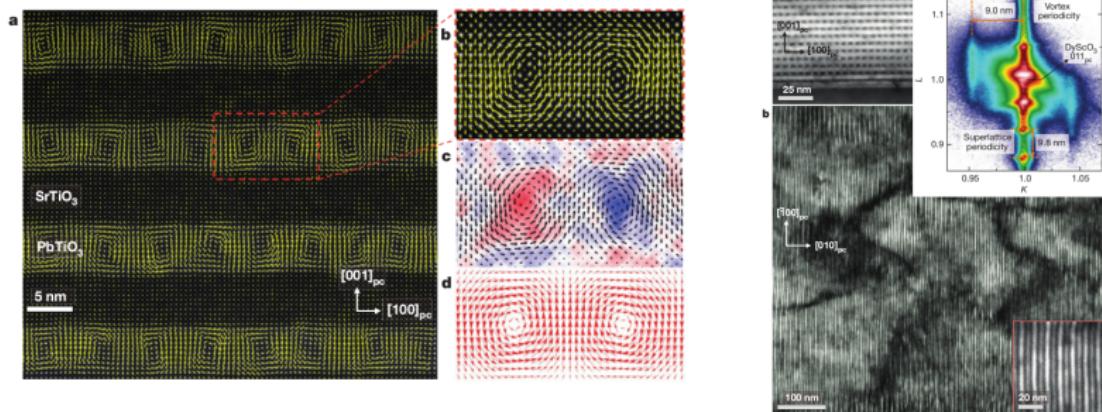


Yadav et al., *Nature*, 530, 198 (2016)

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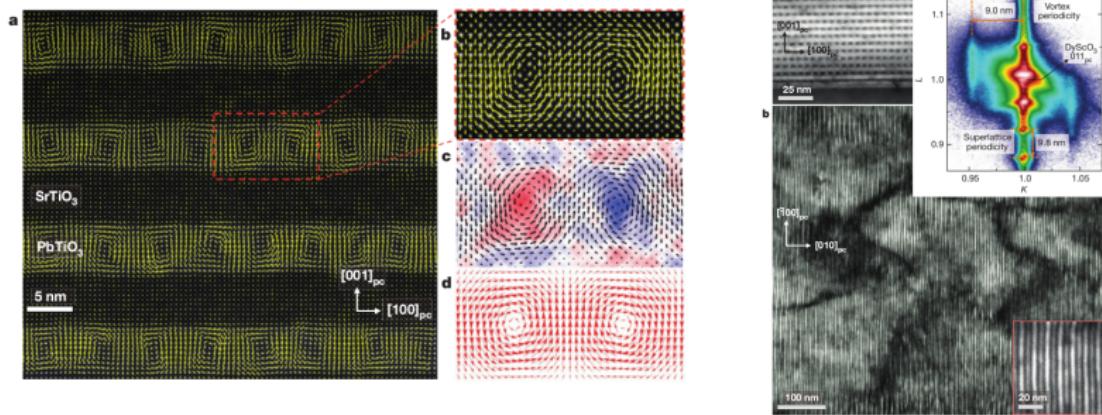


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Grown on DyScO_3

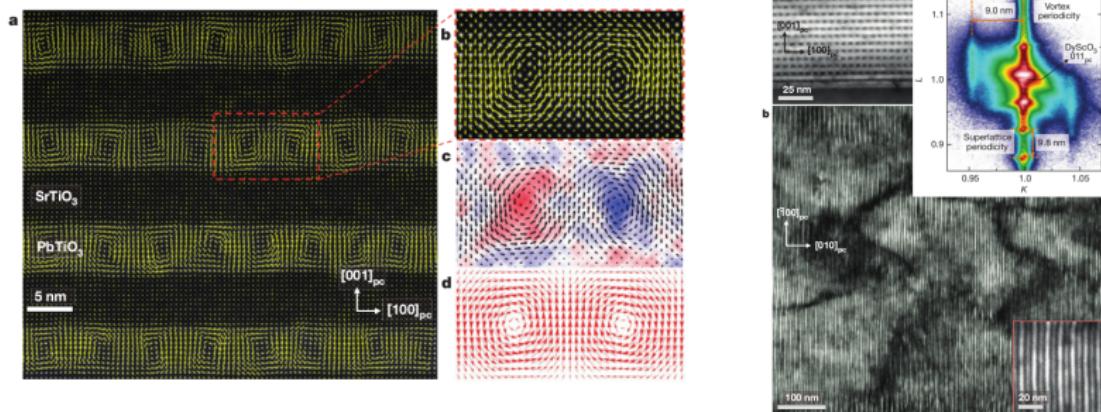
Lateral size vortex-pair $\approx 8\text{nm}$ ($m=10$) - 11.4nm ($m=16$)

Vortex tube extends in the y-direction

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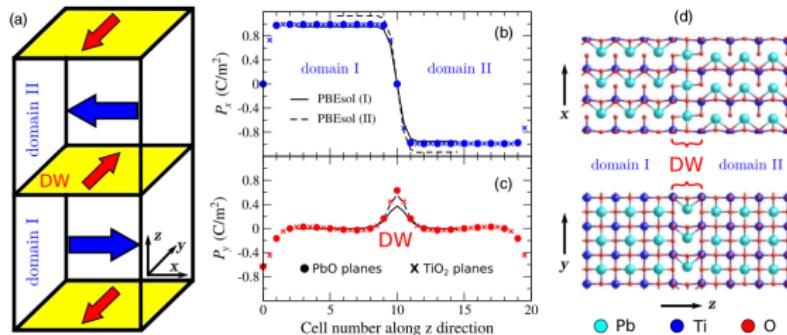
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Little information about polarization in y-direction

Without it: Chirality? topological properties?

Polarization at the domain wall

What happens with polarization at a pure solid's domain wall?



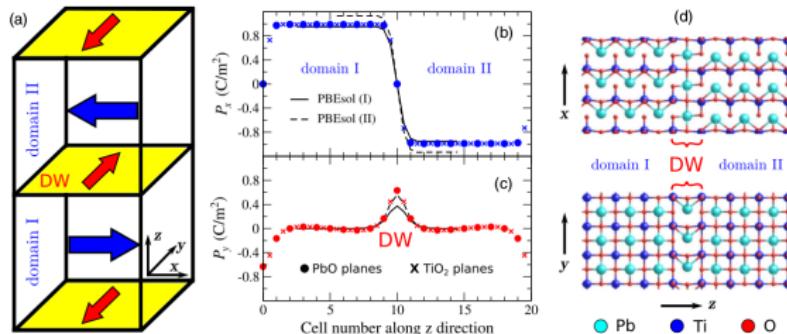
Wojdel and Íñiguez, *Phys. Rev. Lett.*, 112, 247603 (2014)

First-principles show that:

- ① The domain walls are ferroelectric
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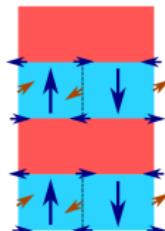
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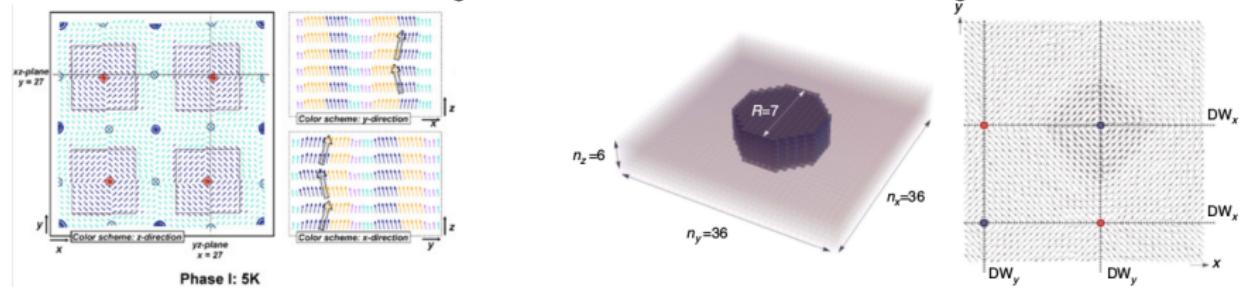
This kind of polarization in the DW:

- ▶ Leads to non-trivial 3D structures
- ▶ Some of them may include topological properties

Is it present in $\text{PbTiO}_3/\text{SrTiO}_3$?

Complex polarization textures in FE nanostructures

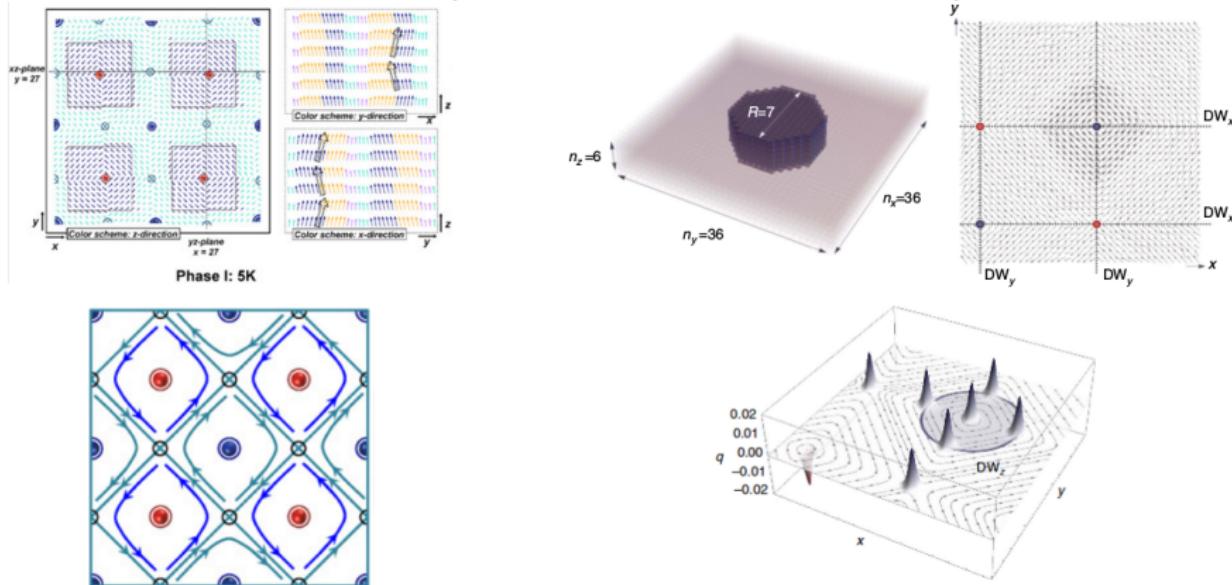
Model Hamiltonian: BaTiO₃ nanowires embedded in SrTiO₃ matrix



Louis et al., *JPCM*, 24, 402201 (2012) Nahas et al., *Nat. Comm.*, 6, 8542 (2015)
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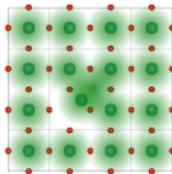
Topological analysis of the structures shows non-trivial phases

What happens in PbTiO₃/SrTiO₃ superlattices?

Problems for carrying out predictive simulations

First-principles

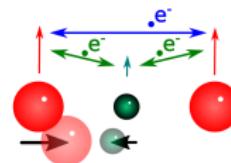
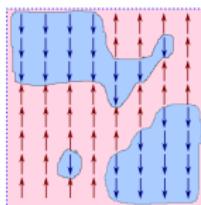
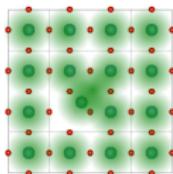
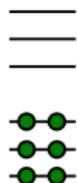
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- ✗ Bad scaling N^3
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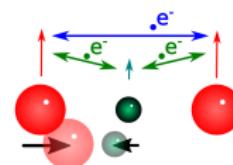
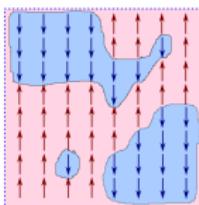
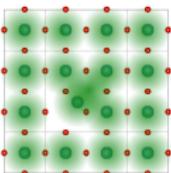
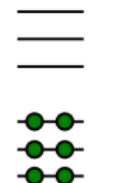
Model Hamiltonians Spins/local dipoles

- ✓ Large systems
- ✓ Temperature
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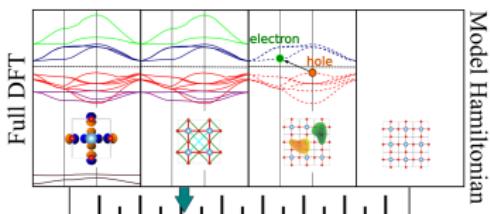
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Can we select the level of fidelity of our calculations?

Can we make it efficient?

Can be reliably constructed from FP?

Second-principles Density Functional Methods

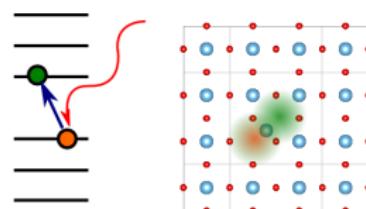
P. Garcia-Fernandez et al., *Phys. Rev. B*, 93, 195137 (2016)

Second-principles DFT

Our starting point is the DFT energy

$$E_{\text{DFT}} = \sum_{j\vec{k}} o_{j\vec{k}} \left\langle \psi_{j\vec{k}} \left| \hat{t} + v_{\text{ext}} \right| \psi_{j\vec{k}} \right\rangle + \frac{1}{2} \iint \frac{n(\vec{r})n'(\vec{r}')}{|\vec{r} - \vec{r}'|} d^3rd^3r' + E_{\text{xc}}[n] + E_{\text{nn}}$$

Response to perturbations usually involves a few active electron/holes



We divide density on reference and deformation densities.

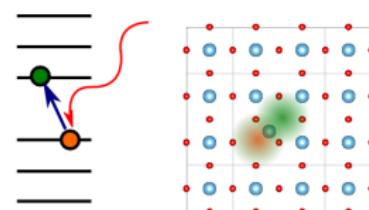
$$n(\vec{r}) = n_0(\vec{r}) + \underbrace{\delta n(\vec{r})}_{\text{electron/holes}}$$

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We divide density on reference and deformation densities.

$$n(\vec{r}) = n_0(\vec{r}) + \underbrace{\delta n(\vec{r})}_{\text{electron/holes}}$$

Only difficulty is the exchange-correlation energy:

$$E_{\text{xc}}[n] = E_{\text{xc}}[n_0] + \int \frac{\delta E_{\text{xc}}}{\delta n(\vec{r})} \Big|_{n_0} \delta n(\vec{r}) d^3r + \frac{1}{2} \iint \frac{\delta^2 E_{\text{xc}}}{\delta n(\vec{r}) \delta n(\vec{r}')} \Big|_{n_0} \delta n(\vec{r}) \delta n(\vec{r}') d^3r d^3r' + \dots$$

SPDFT is a systematic approximation to DFT:

$$E_{\text{DFT}} \approx E = E^{(0)} + E^{(1)} + E^{(2)}$$

P. García-Fernandez et al., *Phys. Rev. B*, 93, 195137 (2016)



Second-principles DFT approach



Material simulations
allow for various approaches

First principles methods are **atomistic** with **flexible detailed bonding**
FP or TB-DFT



Based on atoms

Second-principles DFT approach



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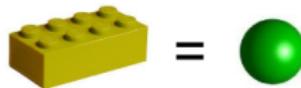
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Second-principles DFT approach



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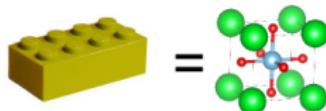


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Accurate properties do not require bond-breaking!



Based on materials

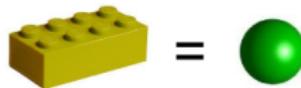
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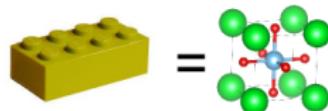


Based on atoms

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Atoms \Rightarrow FP \Rightarrow Materials \Rightarrow SP \Rightarrow Large-scale

Accurate properties do not require bond-breaking!



Based on materials

$$E_{\text{DFT}} \approx \underbrace{E^{(0)}_{\text{lattice}}}_{\text{lattice}} + \underbrace{E^{(1)} + E^{(2)} + \dots}_{\text{electron excitations}}$$

$E^{(0)} \rightarrow$ Accurate description of GS energy surface

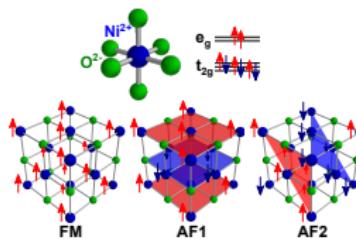
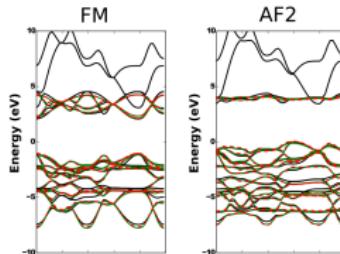
$E^{(1)} \rightarrow$ Bands, metals/insulators, electron-lattice

$E^{(2)} \rightarrow$ Electron correlation: magnetism, doping

Applications of SPDFT



NiO - Insulator with highly correlated electrons:



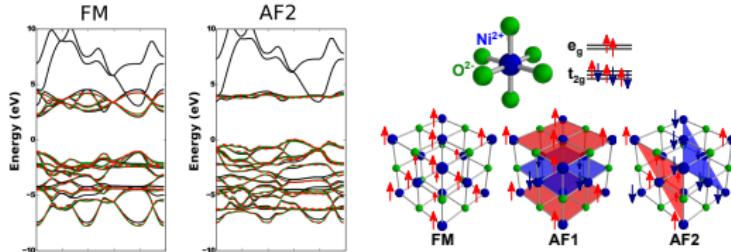
Method	J ₁ (meV)	J ₂ (meV)
neutron	1.4	-19.0
LDA+U	2.6	-17.5
SP-Ni(3d) + O(2p)	3.3	-17.6

Electronic/magnetic properties at DFT level!

Applications of SPDFT



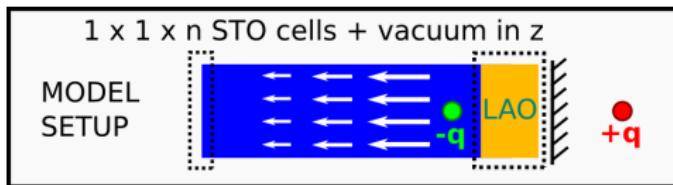
NiO - Insulator with highly correlated electrons:



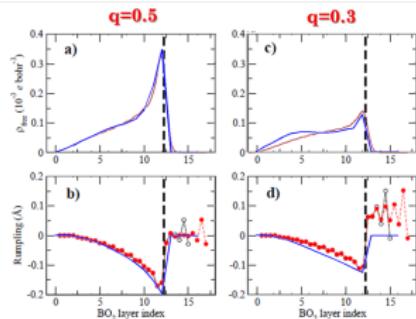
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Electronic/magnetic properties at DFT level!

2DEG at SrTiO₃/LaAlO₃ Interface



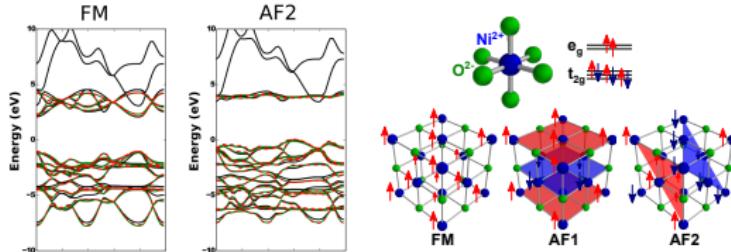
FP → M. Stengel, *PRL*, 106, 136803 (2011)
SPDFT captures doping and lattice screening!



Applications of SPDFT



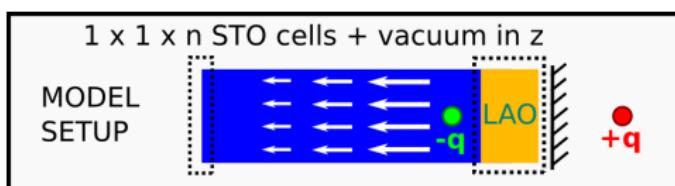
NiO - Insulator with highly correlated electrons:



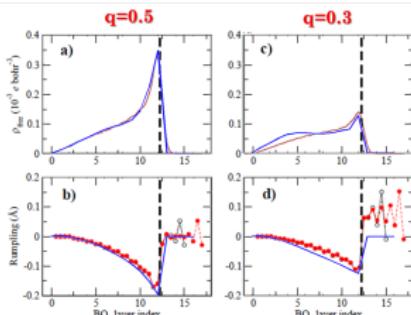
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Electronic/magnetic properties at DFT level!

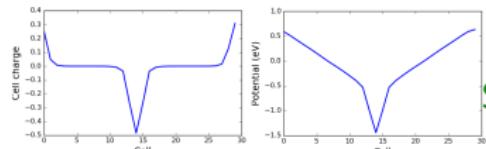
2DEG at SrTiO₃/LaAlO₃ Interface



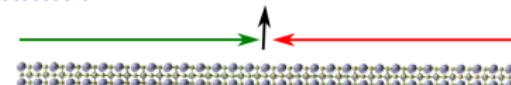
FP → M. Stengel, *PRL*, 106, 136803 (2011)
SPDFT captures doping and lattice screening!



PbTiO₃ conductive/charged domains



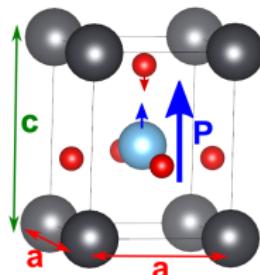
SPDFT → critical size for metastable domains
DFT 1 year running!



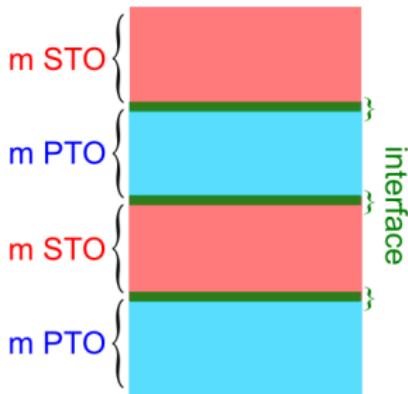
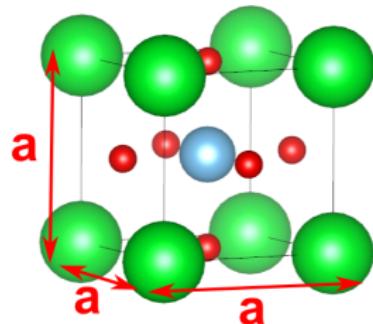
SPDFT in $\text{PbTiO}_3/\text{SrTiO}_3$ interfaces

SrTiO₃ and PbTiO₃ thoroughly tested

PbTiO₃/SrTiO₃ model obtained from pure lattice models



$\Rightarrow \text{PbTiO}_3/\text{SrTiO}_3 \Leftarrow$

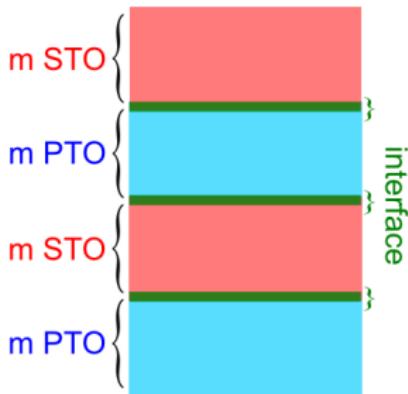
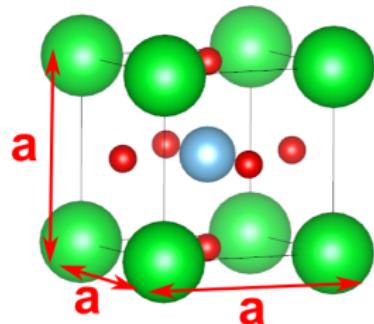
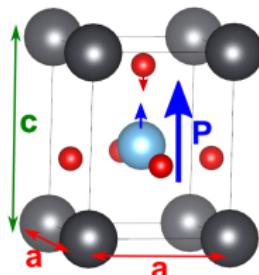


- ▶ Both bulk models are combined into a single one

SPDFT in $\text{PbTiO}_3/\text{SrTiO}_3$ interfaces

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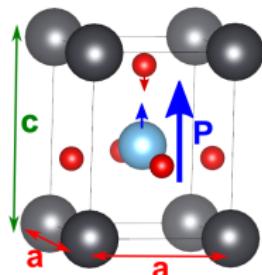


- ▶ Both bulk models are combined into a single one
- ▶ Interface average of local interactions

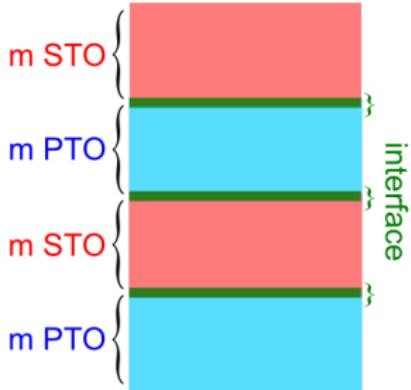
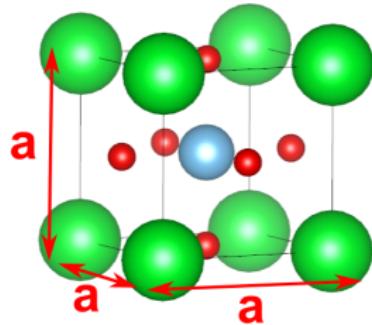
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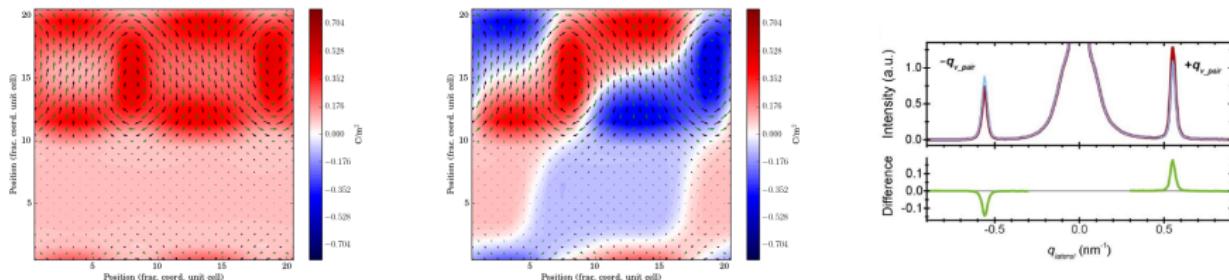
$\Rightarrow \text{PbTiO}_3/\text{SrTiO}_3 \Leftarrow$



- ▶ Both bulk models are combined into a single one
- ▶ Interface average of local interactions
- ▶ Electrostatic parameters (Born charges, dielectric constants) taken so bulk is perfectly reproduced

Simple model yields good agreement with FP and experiment!

Conclusions

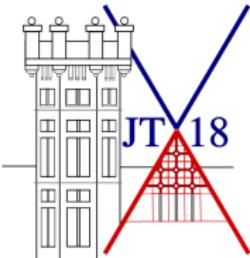


- ① Non-magnetic systems with skyrmion-like textures
- ② At low energies SPDFT predicts many degenerate phases
Some display finite topological charge/Others chirality
- ③ Good detailed theory/experiment agreement
Structure, Vortex size, Chirality

P. Shafer, P. Garcia-Fernandez et al., *Submitted*, , ()

Thank you for your attention!





Electron-vibration phenomena in molecules and solids: Symmetry breaking and beyond

XXIVth Symposium on the Jahn-Teller Effect

24th-29th June 2018, Santander (Spain)

Topical Sessions

- General Theory
- Spectroscopy
- Structure
- Magnetism
- Transition Metal Complexes
- Excitons
- Polarons
- Solid State

Confirmed Speakers

- | | |
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| M.V. Berry | H. Köppel |
| I.B. Bersuker | R. McKenzie |
| E. Coronado | T. Miller |
| A. Datta | R. Sessoli |
| R. Deeth | J. Stanton |
| M. Eremets | |
| J. M. García-Lastra | |
| V. Hizhnyakov | |

